Highly efficient decomposition of pure water into H_2 and O_2 over $NaTaO_3$ photocatalysts

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$NaTaO_3$ with 4.0 eV band gap showed a high activity for the decomposition of pure water into H_2 and O_2 without co-catalysts when it was prepared in the presence of excess Na in order to prevent the formation of defects by the volatilization of Na. When NiO was supported on the $NaTaO_3$ powder, the activity was drastically increased. The quantum yield of the NiO(0.05 wt%)/$NaTaO_3$ photocatalyst was 28% for the water splitting at 270 nm.

Keywords: photocatalyst, water splitting, $NaTaO_3$, tantalate

1. Introduction

The photocatalytic decomposition of water has been studied from a view point of photon energy conversion. TiO_2 [1], $SrTiO_3$ [2–4], $K_4Nb_6O_{17}$ [5], $Na_2Ti_6O_{13}$ [6], $BaTi_4O_9$ [7], ZrO_2 [8], Ta_2O_5 [9] and $K_2La_2Ti_3O_{10}$ [10] photocatalysts have been found to show reasonable activities for the decomposition of water into H_2 and O_2 in stoichiometric amounts. Many of them are titanates. Only $K_4Nb_6O_{17}$ and ZrO_2 can decompose pure water without co-catalyst loading and any additives in the water. Thus, the photocatalyst materials are limited. The authors have recently reported that several tantalates are active photocatalysts for the water decomposition without co-catalysts [11,12]. Among them, $NaTaO_3$ showed much lower activity than $KTaO_3$ [12]. The authors thought, judging from the structure and the luminescent properties of $NaTaO_3$, that the activity of $NaTaO_3$ should have been higher than that obtained at the time. This has stimulated the authors to explore the $NaTaO_3$ photocatalyst further.

In the present paper, it is reported that highly active $NaTaO_3$ is obtained by optimizing the preparation condition and that loading a NiO co-catalyst much increases the activity.

2. Experimental

$NaTaO_3$ powder was synthesized by calcining mixtures of the starting materials Na_2CO_3 (Kanto Chemical, purity 99.5%) and Ta_2O_5 (Rare Metallic, purity 99.99%) at 1420 K for 10 h in air using a platinum crucible. The ratios of Na to Ta in the starting materials were 1 and 1.05. The $NaTaO_3$ powder was washed with distilled water to eliminate the excess Na. NiO co-catalysts were loaded by an impregnation method. The NiO/$NaTaO_3$ powder was calcined at 640 K for 1 h.

The synthesized materials were confirmed by X-ray diffraction (Rigaku, RINT-1400). The surface area was determined by BET measurement (Coulter, SA3100). A diffuse reflection spectrum was obtained by using a UV-vis-NIR spectrometer (JASCO, Ubest-570) and was converted from reflection to absorbance by the Kubelka–Munk method. Photoluminescence was measured at 77 K *in vacuo* using a fluorometer (Spex, Fluoromax).

The photocatalytic reactions were carried out in a gas closed circulation system. The catalyst powder (1 g) was dispersed in distilled water (350 ml) by a magnetic stirrer in a quartz reaction cell. The light source was a 400 W high-pressure mercury lamp (SEN, HL400EH-5). The quantum yield was determined at 270 nm using a band pass filter (half width: 16 nm) by chemical actinometry employing ammonium ferrioxalate. The amount of H_2 and O_2 evolved was determined by using a gas chromatograph (Shimadzu, GC-8A, TCD, Ar carrier).

3. Results and discussion

Figure 1 shows an absorption spectrum at 300 K and photoluminescence spectrum at 77 K of $NaTaO_3$. The excitation spectrum was agreed with the absorption spectra. The energy gap was estimated to be 4.0 eV from the onset of the absorption spectrum. The emission was observed around 460 nm. The Stokes shift was 14000 cm^{-1}. These results fit with those of Wiegel et al. [13]. The emission intensity was relatively high suggesting that the material may be useful as a photocatalyst.

The activities of photocatalytic decomposition of pure water are summarized in table 1. $NaTaO_3$ was able to decompose pure water into H_2 and O_2 in stoichiometric amounts in an experimental error without any co-catalysts

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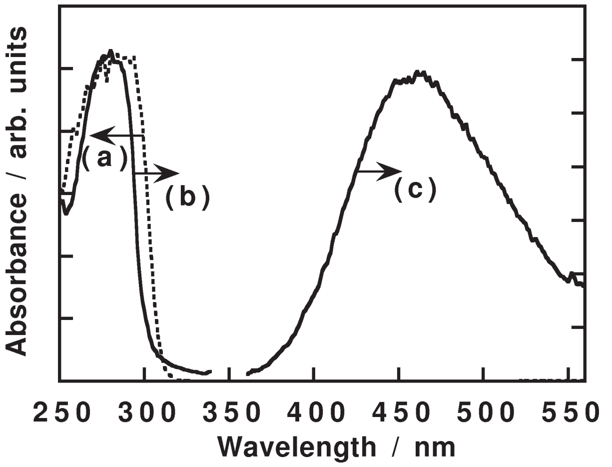

Figure 1. (a) Absorption spectrum at room temperature, (b) excitation, and (c) emission spectra at 77 K of $NaTaO_3$ powder.

Table 1
Effect of excess Na in the preparation and NiO loading on photocatalytic activities for decomposition of pure water over $NaTaO_3$ powder.[a]

Na : Ta[b]	Surface area (m^2/g)	NiO (0.05 wt%) loading[c]	Activity (μmol)/h	
			H_2	O_2
1 : 1	0.53	no	11	4.4
		yes	480	240
1.05 : 1	0.44	no	160	86
		yes	2180	1100

[a] Catalyst: 1 g, distilled water: 350 ml, light source: 400 W high-pressure mercury lamp, reaction cell: inner irradiation quartz cell.
[b] In starting materials.
[c] The NiO-loaded catalyst was calcined at 640 K for 1 h before the photocatalytic reaction.

such as Pt and NiO. However, the activity of $NaTaO_3$ which was prepared in the presence of excess Na (5%) was much higher than that prepared in the stoichiometric ratio. This behavior was reproducible. Only the $NaTaO_3$ phase was observed by XRD measurements of these samples. The surface area was not a major factor for the difference in the photocatalytic activity in the present system. Photocatalytic reactions mainly consist of the following processes: formation of electron–hole pairs by absorption of light, charge separation and subsequent migration of the electrons and holes to active sites, surface reactions, and desorption of products. In the present system, the formation of electron–hole pairs and/or migration of electrons and holes to the surface active sites seem to dominate the reaction rate as observed for photocatalytic reactions in which sacrificial reagents are not employed.

The amounts of H_2 and O_2 evolved increased with irradiation time. However, the activity after 50 h became one third of the initial activity. Moreover, the photocatalytic activity decreased even when the catalyst was dispersed in pure water under dark. XRD measurements revealed that the $NaTaO_3$ powder was not changed after the photocatalytic reaction. These results suggest that the deactivation be due to the elution of surface Na and the activity depends on the surface defects. When $NaTaO_3$ was prepared at 1420 K of the high temperature in the stoichiometric ratio of Na to Ta, Na defects might be formed by the volatilization. In contrast, the formation of such a defect can be suppressed in the presence of excess Na in the preparation. On the other hand, the excess Na may work as a flux in the preparation resulting in an increase in the crystallinity of $NaTaO_3$. Less defects and higher crystallinity lead to higher photocatalytic activity, because the recombination between photogenerated electrons and holes at the defect is suppressed. This seems to be the reason why the activity of $NaTaO_3$ prepared in the presence of excess Na (5%) was much higher than that prepared in stoichiometric ratio.

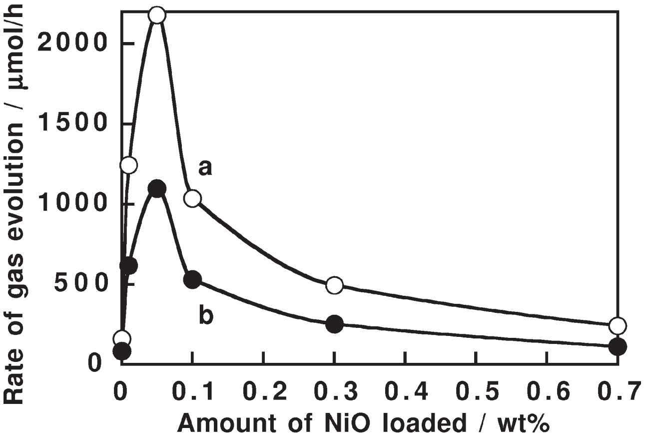

Figure 2. Dependence of the photocatalytic activity for decomposition of pure water over NiO/$NaTaO_3$ upon the amount of NiO loaded ((a) H_2, (b) O_2). Catalyst: 1 g; distilled water: 350 ml; light source: 400 W high-pressure mercury lamp; reaction cell: inner irradiation quartz cell.

Figure 2 shows the dependence of the photocatalytic activity on the amount of NiO loaded as a co-catalyst. The photocatalytic activity was much increased by the NiO loading. In general, the pretreatment of H_2 reduction and subsequent O_2 oxidation is indispensable for the NiO-loading photocatalysts showing the high activity [3–5,9,10]. In contrast, such a pretreatment was not necessary for the $NaTaO_3$ photocatalyst as well as other tantalates [11,12]. The optimum amount of NiO was 0.05 wt%. The activity decreased when the amount of NiO was larger than 0.05 wt%. This behavior has usually been observed in the case of co-catalyst-loaded photocatalysts [5,10]. The color of NiO is gray. The excess amount of NiO shields incident light and unnecessarily covers the $NaTaO_3$ surface resulting in the decrease in the activity in the region.

The quantum yield of the NiO(0.05 wt%)/$NaTaO_3$ photocatalyst was 28% at 270 nm. This value is considerably high for the decomposition of pure water into H_2 and O_2 in stoichiometric amounts. The effect of scattering is not taken into account. The actual quantum yield will be larger than 28% if the scattering effect is considered. However, it is actually difficult to estimate the scattering effect. The photocatalytic activity of NiO(0.05 wt%)/$NaTaO_3$ gradually decreased although the high activity was maintained even

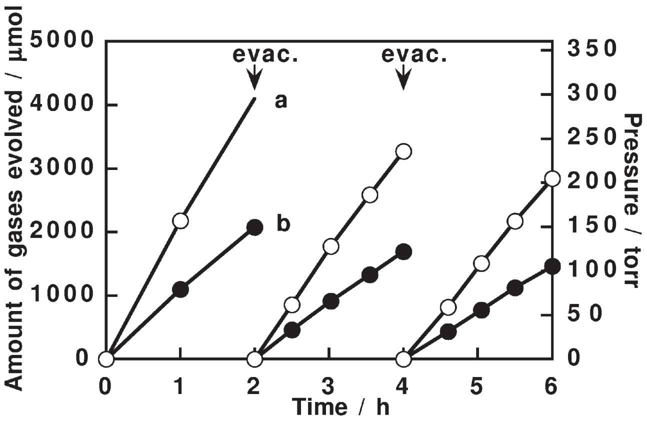

Figure 3. Photocatalytic decomposition of pure water over NiO(0.05 wt%)/$NaTaO_3$ ((a) H_2, (b) O_2). Catalyst: 1 g; distilled water: 350 ml; light source: 400 W high-pressure mercury lamp; reaction cell: inner irradiation quartz cell.

after 6 h of the reaction time as shown in figure 3. This is probably due to the elution of Na as observed for native $NaTaO_3$ photocatalysts. However, the total amounts of H_2 and O_2 evolved were 10 and 5.2 mmol after 6 h of irradiation, respectively. The amounts of $NaTaO_3$ and NiO in 1 g of the NiO(0.05 wt%)/$NaTaO_3$ photocatalyst were 4 mmol and 6.7 μmol, respectively. Moreover, the turnover number of reacted electrons or holes per one Ta atom on the surface amounted to ca. 4000. The total amount of Ta on the surface was estimated from the surface area and assuming the (010) face. It is not guaranteed that all Ta atoms on the surface are active sites as commented. Therefore, the TON is least estimated. This rough calculation is enough to indicate that the decomposition of water proceeded photocatalytically on the nontreated NiO(0.05 wt%)/$NaTaO_3$ photocatalyst.

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